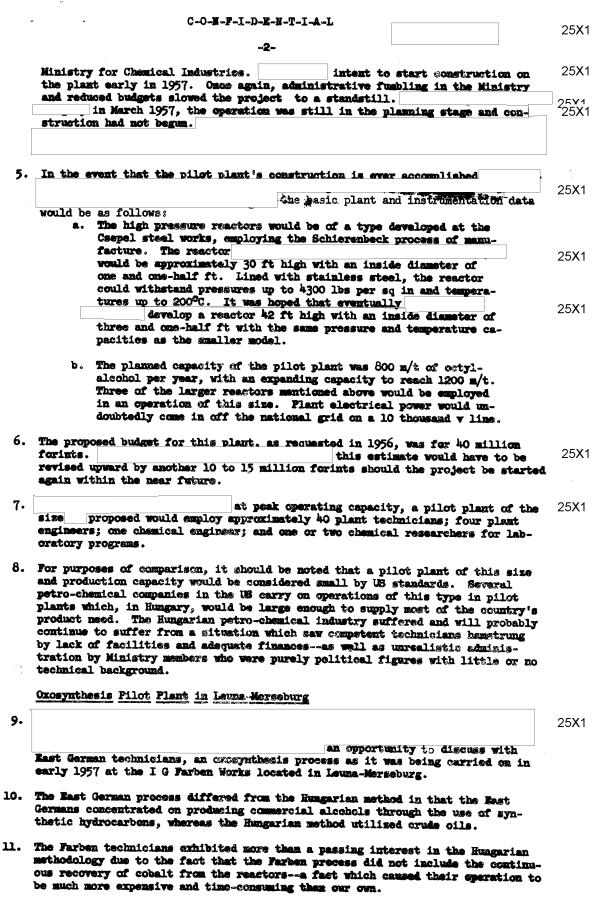
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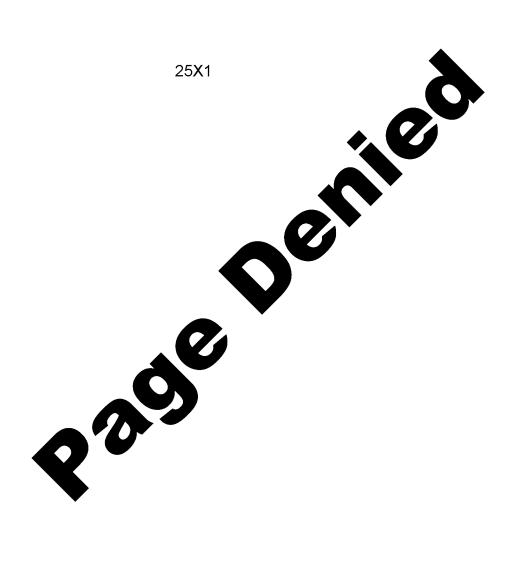


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12.	no opportunity to discuss the Farben plant operation or espacity at	25 X 1
	the East Germans	25X1
	had produced only test quantities of high molecular weight alcohol for use in plasticizers and detergents. Their 1956 production did not exceed 20 m/t.	
13.	Since both the East German and Hungarian processes for synthesizing alcohols depended on raw materials indigenous to the respective areas, coal on the one hand, crude oil on the other, I could foresee no changing of processing techniques by either scientific group. The East Germans felt that while their own system was more expensive than that employed by the Hungarian chemical industry, it best suited their facilities and purposes.	
14.	One other noteworthy fact concerning the development section of the Farben works in Leuna-Merseburg was the very small proportion of professional technicians to plant labor. The ratio of professional engineers and experienced technicians to skilled and unskilled laborers at the East German Farben plant was one technician to 70 laborers, as opposed to a ratio of one to 18 in West German Farben complexes. The underlying explanation for this situation is, of course, the more lucrative salaries effered to scientific personnel in the Western European countries.	
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ACTA CHIMICA

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DIRECT SYNTHESIS OF ALCOHOLS FROM OLEFINS WITH A MIXTURE OF CARBON MONOXIDE AND HYDROGEN

MODIFIED OXO-PROCESS
J. BERTY and L. MARKÓ

(Hungarian Oil and Natural Gas Research Institute, Budapest- Vessprém)

Received August 19, 1952

In the Oxo-process olefins react with carbon monoxide and hydrogen to produce aldehydes:

This synthesis is a well established process for the commercial production of higher alcohols and the aldehydes formed are therefore directly converted to alcohols in a second reaction without previous purification of the product.

Up till now solid catalysts containing cobalt have been used for the commercial Oxo-process, like the ordinary Fischer. Tropsch catalyst or silicagel with cobalt. The reduction of the aldehydes was carried out with copper-chromium catalyst when the starting material was a Fischer—Tropsch olefin distillate containing no sulphur. When processing olefins resulting from the cracking of straight run distillates, sulphur resistant nickel and tungsten catalysts were applied. The hydrogenation of sulphur containing aldehydes presents some difficulties, especially because the aldehydes enter many side reactions at the relatively high temperature at which the sulphur resistant catalysts become sufficiently active and the yields are therefore rather low.

The olefinic raw materials for the Oxo-process, especially the mixtures which are liquid at room temperature, contain other hydrocarbons beside olefins, such as paraffins, naphthenes and in some cases also aromatics. Their separation from the aldehydes is very difficult, resulting in a considerable decrease in the aldehyde yields. Therefore, even when the process is used to produce aldehydes, the crude oxo-aldehydes are first reduced to the respective alcohols which, after separation from the non-olefinic hydrocarbons, are again oxidized to aldehydes.

It was already assumed by the research workers of the sRuhrchemies that even in the presence of solid catalyst the active catalyst was cobalt which acted in homogeneous phase. This fact was later fully investigated by Adkins and Krsek[1] who succeeded in accomplishing the aldehyde synthesis by using only a homogeneous phase cobalt catalyst.

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In the course of the conversion into aldehydes other products are also formed, including 10—20 per cent of the corresponding alcohols. This fact of considerable practical importance has only been investigated recently. I. Wender and co-workers have proved [2,3], that these alcohols are formed in a homogeneous catalytic reaction from the primary products, the aldehydes. The catalyst, probably cobalt carbonyl hydride HCo(CO)₄ formed from the cobalt compounds used, is sulphur resistant and active only at high carbon monoxide partial pressures. The reduction needs somewhat higher temperatures than the Oxo-process (the above mentioned investigators carried out their experiments at an average temperature of 180—185. C) but the other reaction conditions are identical. In this manner it has become possible to convert n-butyraldehyde into n-butylalcohol with a yield of 72%.

On the basis of the above, the Oxo-synthesis and the subsequent reduction can be carried out in one step in the operation named adirect alcohol synthesiss. Starting from octene-l, a mixture of isomer nonyl alcohols has been produced in one step (ibid) with 61% yield.

G. Natta and co-workers [4] also investigated the direct alcohol synthesis. Working without hydrogen in the presence of secondary alcohols, they succeeded in getting a product which consisted of 70 per cent alcohols. The one-one mole hydrogen necessary for both the Oxo-process and the reduction was provided by the secondary alcohol, which in turn was converted into ketone.

The importance of the direct alcohol synthesis consists in the fact that the reaction which has hitherto been carried out in two steps, can now be accessplished in a single operation. By means of this, the rather delicate reduction epopation — especially with raw materials containing sulphur — can be avoided. From this point of view, however, the disadvantage of the 72% yield achieved by I. Wender and co-workers is that it makes separation very difficult, Yet, taking the advantages into consideration, it seemed useful to take up the disadvantage alcohol synthesis and, first of all, to clarify the possibility of increasing the alcohol yield, in order to make the separation practicable, and by means of this to make the process possible on an industrial scale. In the course of our work carried out in the Hungarian Petroleum and Natural Gas Research Institute in connection with the Oxo-process, we, therefore, soon took up the investigation of the direct alcohol synthesis, this being in our opinion the most practicable way towards the realisation of the process.

In order to investigate the influence of temperature, the most important variable at the Oxo-process, three series of experiments have been carried out.

1. Homogeneous catalytic reduction of butyraldehyde:

$$CH_3 - CH_3 - CH_3 - CH_3 - CH_0 + H_0 \xrightarrow{CO} CH_0 - CH_3 - CH_3 - CH_3 - CH_3 OH$$



2. Oxo synthesis and direct alcohol synthesis with evclohexene:

$$+ CO + 2H_0 \xrightarrow{HCo(CO)_4} H - CH_0OH$$

3. Oxo synthesis and direct alcohol synthesis with cracked gasoline:

$$R - CH = CH_1 + CO + 2H_2 \xrightarrow{HCo(CO)_A} R - CH_1 - CH_2 - CH_2OH.$$

The experimental conditions as well as the results are shown in Tables 1, 2 and 3. For the reduction percentage with butyraldehyde see Figure 1. The reduction percentage and the quantity of gas reacted (mole gas for mole olefin) at the experiments with cyclohexene and cracked gasoline can be seen on Figures 2 and 3, respectively. The extent of the reduction was measured by the relative alcohol content of the oxygenated compounds, the aldehydes and alcohols, this value giving more characteristic results than the alcohol content of the end product in percents. The reason for this is that the removal of cobalc, which is necessary before the analysis, irreproducibly alters the absolute alcohol content, whereas the alcohol-aldehyde ratio does not change essentially. Therefore, the latter value is always shown in the figures. In the experiments with butyraldehyde the quantity of gas which reacts is not shown in the figure because, as can be seen on Table 1, this is invariably higher than is to be expected in accordance with the reduction. Obviously, some kind of a side reaction takes place, and this is still being investigated.

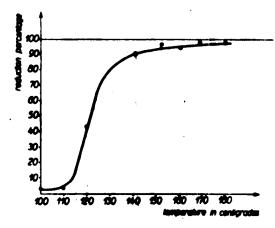


Fig. 1

Hemogeneous catalytic reduction of butyraldehyde Reduction percentage as a function of temperature

Catalyst: 3,2 mole per cent cobalt stearate, calculated for the aldehyde

Pressure: 160—200 atm.
Gas composition: 2 H₀+1 CO
Reaction time: 100 minutes

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The following conclusions may be drawn from the diagrams:

Under the experimental conditions of the Oxo-process, n-butyraldehyde can be reduced at 150—155° C practically up to 100 per cent. This 100 per cent reduction, however, does not mean that the reaction product consists of butyl-

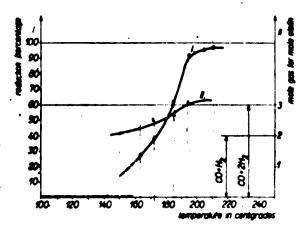


Fig. 2

Direct alcohol synthesis with cyclohexene

Reduction percentage (I) and gas consumption (II) as a function of the temperature

Catalyst: 0,8 mole percent cobalt stearate, calculated for the olefin Pressure: 150--200 atm.

Pressure: 150-200 atm. Gas composition: $2H_g+1$ CO Reaction time: 30 minutes

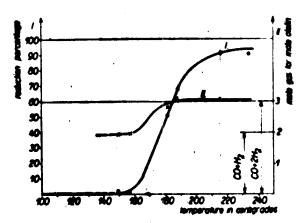


Fig. 3

Direct alcohol synthesis with cracked gaseline

Reduction percentage (I) and gas consumption (II) as a function of the temperature Catalyst: 1,1 mole percent cobalt stearate, calculated for the olefin Pressure: 130—200 atm.

Pressure: 130—200 atm.
Gas composition: 2H_a+1 CO
Reaction time: 60 minutes

DIRECT STRUMBIS OF ALCOHOLO PROM CLEPIES WITH A MIXTURE OF CARBON MONOXIDE AND MYDROGEN

TABLE 1

Reduction experiments with butyreldehyde

Charge steck: 0,5 mele=36 g butyraldehyde in 110 ml motor spirit

Catalyst: 3,2 mole % Co stearsts calculated for the aldehyde

Gas composition: H₀: CO=2:1 Reaction time: 100 minutes Pressure: 160—200 atm.

	Tump. *C	Command gap in moles	End product		
No. of experiment			Aldebyde	· Alcahal %	Absolut absolut + absolut %
V. 14	100	0,61	7,84	0,33	4,1
V. 10	110-112	0,77	7,81	0,31	3,9
V. 13	120	0,61	8,72	6,60	43,0
V. 11	140-142	0,64	1,50	13,3	90,0
V. 17	149—155	1,47	. 0,64	17,5	96,4
V. 12	160	0,99	0,90	15,8	94,8
V. 16	167170	1,00	0,29	17,8	90,6
V. 15	178—190	1,05	0,28	19,5	96,8

TABLE 2

Direct alcohol synthesis with cyclohenene

Charge stock: 0,2 moles=16,4 g cyclohexene in 400 ml motor spirit

Catalyst: 0,8 mole % Co stearste calculated for elefin

Gas composition: H₄: CO=2:1

Reaction time: 30 minutes Pressure: 150-200 atm.

•	Tump. °C	Construct gas in makes	End product		
No. of experiment			Aldahyda	Alrebel	Alocked dealed + delety %
V. 10a	100—109		_		-
V. 11a	138147	-	-		_
V. 23	159-167	0,46	8,41	1,37	28,7
V. 11b	165199	0,52	2,24	3,56	80,8
V. 76	185	0,54	1,32	2,78	62,3
V. 13	190-200	0,63	9,54	5,72	91,5
V. 14	203-205	0,88	0,38	8,10	95,6
V. 16	205—214	9,64	0,24	5,90	96,3

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TABLE 3

Direct alcohol synthesis with cracked gasoline

Charge stock: 37 g cracked gasoline containing 0,15 mole olefin in 370 ml motor spirit

(atalyst: 1.1 mole % Co stearate calculated for olefin

Gus composition: H₂: CO=2:1
Reaction time: 60 minutes
Pressure: 130—200 atm.

			End product		
No. of experiment	Tump. °C	Commend gas in mobile	Aldebyde %	Alrehal %	Alcohol alcohol + aldohydo %
١. 20	124-134	_			-
V. 21	146—155	9,30	4,75	0,11	2,3
V. 22	155160	0,30	5,22	0,06	1,1
V. 17	179185	9,42	2,87	3,06	51,5
V. 19	186195	0,46	1,72	3,68	68,2
V. 24	214-222	9,47	0,47	4,97	91,5
V. 31	230—242	0,45	0,47	4,41	90,5
	1 .	1	1	i	ı

alcohol only, as C_s and higher alcohols are also present. These higher alcohols are formed from higher aldehydes which in turn are formed from butyraldehyde as a result of aldol conversion. There are, however, hardly any carbonyl compounds in the end product.

The minimum temperature at which the formation of cobalt carbonyl and the Oxo-process started, respectively, was in the course of our direct synthesis experiments approximately 145° C. At this temperature practically no alcohol is produced, either with cyclohexene, or with cracked gasoline. By raising the temperature, the relative alcohol content increases, first slowly, then at a rapid rate, and reaches more than 95 per cent at 200—210° C with cyclohexene, and 90 per cent at 220° C with eracked gasoline. Alongside with the increase of the extent of reduction the gas quantity used in the individual experiments also increases from quantities in accordance with the Oxo-reaction, CO+H₂ (2 moles), to the quantity corresponding to the 100 per cent reduction, CO+2H₂ (3 moles), and even somewhat above this. The gas consumption points to a more extensive reduction than berne out by the results. This latter fact may be caused by some side reaction in which additional gas is absorbed, possibly the homologue formation of the alcohols:

$$-CH_{g}OH + CO + 2H_{g} \longrightarrow -CH_{g}-CH_{g}OH + H_{g}O$$
 (5)

Comparison of the curves reveals that the reduction of higher aldehydes is carried out with greater difficulty than that of the lower members of the series.

It can be shown by means of approximate thermodynamic calculations $|M_{1500~K}| + 0.8$ Kcal/mole, $K_p = K_n$. $P^{(.1n)} = 0.37$ that under such reaction circumstances equilibrium is shifted towards the formation of the alcohol practically to 100 per cent. It follows from the above that in the course of our experiments carried out for the same length of time no equilibrium was reached and the increased reduction at higher temperatures is due to increased reaction rates brought about by them. It is therefore probable that by an adequate increase in the duration of the reaction, an adequate reduction can be accomplished at lower temperatures as well. In spite of the above, the high temperature reaction is more interesting from the point of view of commercial realisation, due to better output. Corrosion of the materials of equipment must, however, be taken into consideration when applying higher temperature.

Further, we have investigated the correlation between the temperature and the total quantity of the oxygenated compounds formed. Certain investigators (Roelen [6]) are of the opinion that the greatest drawback to the direct alcohol synthesis consists in the olefins hydrogenating to paraffins due to the high temperatures required, without previously participating in the Oxoprocess. Contrary to this opinion, in our experiments at higher temperatures, where conversion to alcohol was nearly complete, 3 moles gas were used for 1 mole olefin. Had a simple hydrogenation of the olefin taken place, the quantity of the consumed gas should have been much less, as only 1 mole gas is used for 1 mole olefin in case of hydrogenation. Consequently, no olefin saturation of importance took place in our experiments.

This assumption is also supported by the fact that in the liquid product the yield of oxygenated compounds calculated for the olefin was constant within the range of experimental and analytical errors.

The olefin saturation mentioned by certain investigators probably occurs under heterogeneous catalytic conditions. The absence of the saturation reaction of the olefins in our homogeneous catalytic reaction was to be expected, as, under those circumstances, the aldehyde formation in the Oxo-process is instantaneous and there is no time left for the hydrogenation of the olefin.

EXPERIMENTAL

The experiments were carried out in an electrically heated rocking autoclave of 870 ml. The necessary pressure was produced by means of a Hofer-type compressor. A thermocouple reaching into the autoclave was used for temperature measurement and the pressure recorded by a disk recording gauge.

The butyraldehyde was prepared from butyl alcohol by exidation with potassium bichromate [7] and the cyclohexene from cyclohexanol by dehydration with sulphuric acid[8]. Both materials were fractionated in a Widmer column. The purity of the products exceeded 96 per cent in every experiment. The data of the cracked gasoline were as follows:

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Initial beiling point 21° C Composition: 28% aromatics End beiling point 147° C 40% olefins

Average molecular weight 100 30% paraffins-naphthenes

No. of carbon atoms C₄-C₉ Spec. gravity 0,7214

The entalyst consisted exclusively of cobalt stearate and no carrier or metallic cobalt was used. The cobalt stearate was produced from cobalt acetate by fusing it with the equivaent quantity of stearic acid and subsequently distilling off the acetic acid and crystal water.
Cobalt stearate is easily soluble in organic solvents, like gasoline, and its application is therefore rather simple.

1)

Direct elechol synthesis with systehausne

14,6 g cyclobezone (0,30 mole) and 1 g cobalt stearate were dissolved in 400 ml motor spirit and placed into the anteclave. The strong dilution of the elefin served the purpose to keep the temperature of the reaction mixture practically constant in spite of the high reaction rate and exothermic character of the Oxo-process. Before using such highly diluted mixtures it often occurred that due to the large amount of heat set free the temperature was raised even by 50°C, as a result of which the experiments became irreproducible. The dilution does not interfere with the amount course of the reaction.

The autoclave was charged to 40 atm. with carbon monoxide and then to 120 atm. with hydrogen, which corresponds to about 2,2 moles gas, equivalent to a fourfold excess. The autoclave was then heated to the necessary temperature without shaking. Shaking was only started when the temperature had become constant. Generally a very quick, almost instantaneous pressure drop took place, and the consumed gas was somewhat in excess of the quantity necessary for the aldebyde fernation. The shaking was continued for 30 more minutes, during which period the pressure drop was much slower. Shaking was then discentinued and the apparatus cooled. The pressure was again recorded at room temperature, and the amount of gas consumed by the reaction calculated from the difference between the starting and the end pressures.

The colour of the end product ranged from yellow to dark brownish red but it became much darker in all cases after storage in air. This is probably due to the gradual conversion of the colourless coholt carbonyl hydride to coholt carbonyl.

Refere earrying out the analysis, the disselved cobalt compounds had to be removed from the end product, because they interfere with the determination. This was achieved by stirring with 5% subplusis sold at 50 °C, when the cobalt compounds were converted into cobalt subplute, which imparts a pink colour to the subpluric acid solution. After separation and drying with lime hydrate the end product is ready for analysis. The determination of the carbonyl compounds was carried out by the hydroxylamine chlorohydrate method[9], and that of the alcohols with phthalic aphydide[10]. The advantage of the latter as against the acetic anhydride method is that it is not influenced by aldehydes.

We wish to express our thanks to Director M. Fround for his valuable assistance and to the laboratory personnel whose ecoperation mode it possible to compile the above data.

SUMMARY

On the basis of the above described experiments, increasing the temperature of the Oxo-process resulted in the synthesis of alcohols at 96 per cent yields using cyclohexene and 90 per cent yields with cracked gasoline by means of the direct alcohol synthesis. During the reduction carried out simultaneously with the Oxo-process the olefins were not hydrogenated to paraffins and the convenient to expressed companyle was close to 100 per cent.

conversion to exygenated elempounds was close to 100 per cent.

Thus the fermation of alcohols from olefins by direct alcohol synthesis has been made practically complete and the process is ready for development on an industrial scale.

STREET SYNTHESIS OF ALCOHOLS FROM OLEPINS WITH A MIXTURE OF CARBON MONOXIDE AND MYDROGEN

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ПРЯМОЙ СИНТЕЗ АЛКОГОЛЕЙ ИЗ ОЛЕФИНОВ ПРИ ПОМОЩИ ГАЗОВОЙ СМЕСИ ОКИСИ УГЛЕРОДА И ВОДОРОДА

Й. Берти и Л. Марко

(Исследовательский институт нефти и природного газа, Будапешт Веспрем.) Поступило: 19. VIII. 1952.

Резюме

В процессе работы над оксосинтезом гомогенной фазы мы исследовали, какое н шяние оказывает изменение температуры с одной стороны на однородное каталитина оксосинтез циклогексена и ческое носстановление бутиральдегида, а с другой крекингбензина. Нами установлено, что бутиральдегид при температуре 150 155 С может быть практически восстанивлен полностью, т. е. на 100%, ов. Затем установлено, что из циклогексена при температуре 200—210 С в один прием можно получить 95%,-ный выход алкоголя, а из крекингоензина при температуре 200 С 90%,-ный выход.

далее нами установлено, что с повышением температуры не снижается процент использования исходного материала, т. е. олефины не гидрогенизируются в парафины. Следовательно, этот примой синтез алкоголей может быть осуществлен как с технологической, так и с экономической точек зрения. В случае переработки содержащих серу ввиду возможности избежать необходимости применения довольно тонкого процесса контактно-каталитического восстановления он может быть легче осуществлен, чен первоначальный двухступенчатый процесс.

UNMITTELBARE SYNTHESE VON ALKOHOLEN AUS OLEFINEN MITTELS EINES GASGEMISCHES AUS KOHLENMONOXYD UND WASSERSTOFF

J. BERTY UND L. MARKÓ

(Vorsuchsinstitut für Mineralöl und Erdgas, Budupest I essprém) Eingegangen am 19. August 1952

ZUSAMMENFASSUNG

Im Laufe ihrer Arbeit untersuchten die Verfasser, welchen Einfluss die Anderung der Temperatur einerseits auf die homogene katalystische Reduktion von Butyraldehyd mittels eines Gemisches von Kohlenmonoxyd und Wasserstoff anderseits auf die Oxosynthese mit Cyklohexen und Krackbenzin ausübt. Es wurde festgestellt, dass sich Butyraldehyd bei 150 155 C praktisch 100° o-ig reduzieren lässt, sowie dass sich aus Cyklohexen bei 200 210 C mit einer Ausbeute von 95% und aus Krackbenzin bei 220 °C mit einer Ausbeute von 90% Alkohole in einer einzigen Operation herstellen lassen.

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Die Verfasser haben nachgewiesen, dass bei Erhobung der Temperatur die auf das Olefin berechnete Ausbeute nicht abnimmt, d. h., dass die Olefine nicht zu Paraffinen hydriert wirden. Diese direkte Alkoholsynthese kann daher sowohl technisch, als auch wirtschaftlich gleich gut ausgeführt werden und lässt sich im Falle der Verarbeitung von schwefelhaltigen Olefinen leichter verwirklichen, als das ursprüngliche zweistufige Verfahren, da hier die heikle Operation der kontaktkatalytischen Reduktion vernieden wird.

Jozsef Berty, Magyar Ásványolaj és Földgáz-Kísérleti Intézet, Veszjirém

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